Laser alloyed cadmium layers on GaAs

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Optical microscopy, Rutherford backscattering (RBS) and electrical measurements have been performed on laser irradiated cadmium layers on GaAs. RBS measurements show that cadmium diffuses into the GaAs and occupies substitutional sites, but electrical measurements are difficult to carry out and may be affected by decomposition of the GaAs surface caused by the laser anneal.

1. Introduction
Although the idea of laser alloying is not new [1], there are very few references to its use with GaAs. The most recent papers describe the formation of ohmic contacts by laser annealing films based on Au–Ge alloys which had been deposited on to n-type GaAs [2–4]. The formation of p^+ layers by laser alloying magnesium [5] and zinc [6] have also been discussed in the literature. In this paper we present the results of a study of laser alloyed cadmium layers on GaAs and make a comparison with previous work on the Zn/GaAs system [6].

2. Experimental method
The experimental methods and materials used have been described in a previous paper [6] and so here we will present only a brief summary of the method used. $4 \times 4 \, mm^2$ samples of bulk (1 0 0) semi-insulating (SI) and bulk (1 0 0), n-type GaAs ($n = 1 \times 10^{17} \, cm^{-3}$) were coated with about 120 nm cadmium. The cadmium was deposited on to the n-type GaAs by evaporation through 0.5 mm diameter holes in a steel mask, whereas the SI material had its top surface completely coated.

Laser annealing was performed in air with single, 25 nsec pulses from a Q-switched Ruby laser of energy density in the range 0.2 to $1.6 \, J \, cm^{-2}$. An L-shaped quartz rod was used to homogenize the laser beam.

Rutherford backscattering (RBS) using 1.5 MeV He^+ ions was used to examine the samples before and after etching the residual cadmium from the SI GaAs using HCl. Four-point probe resistivity and Van der Pauw measurements of resistivity, Hall coefficient, carrier concentration and mobility profiles and $I-V$ measurements were performed using the methods described previously [6].

3. Results
3.1. Nomarski interference microscopy
For a laser energy density of up to $0.3 \, J \, cm^{-2}$ the surface of the cadmium layer contained some small brown spots which we believe correspond to melting of the cadmium (Fig. 1a). Following removal of the cadmium, the GaAs surface was smooth (Fig. 1b) which may indicate that the GaAs did not melt. For an energy density greater than $0.3 \, J \, cm^{-2}$ (Fig. 1c), some pits appear whose density and size increase with increasing energy density (Fig. 1d). This phenomenon seems to be associated with melting of the GaAs. Finally, for the highest energy density of $1.5 \, J \, cm^{-2}$ there are many large ripples present (Fig. 1e) indicating that the whole surface has melted and probably suffered from thermal etching.

3.2. Rutherford backscattering
Because of the large difference between the atomic mass of cadmium and those of arsenic and gallium, it is possible to use RBS to study the alloying of cadmium in GaAs. Various measurements were performed on annealed samples either before removal of the remaining cadmium or after removal of the cadmium by etching in HCl. Fig. 2 shows spectra corresponding to GaAs samples which were not etched after laser irradiation. For the unannealed sample ($0 \, J \, cm^{-2}$), there is a peak between channels 400 and 425 corresponding to the as-deposited cadmium layer. The thickness of this layer calculated from the RBS spectra is in good agreement ($\sim 1200 \, nm$) with the results obtained using a Rank Taylor Hobson talystep. The cadmium yields obtained following laser irradiation (Fig. 2) are identical within experimental error for both aligned and random spectra. The areas beneath these cadmium peaks and their heights decreased following irradiation. Since the areas are proportional to the quantity of cadmium residing on or near the GaAs surface, then this result indicates that cadmium is lost by evaporation from the surface.

The high value of χ_{min} for the non-etched material is due to dechannelling of the helium beam as it passes through the cadmium layer. For low energy densities ($\sim 0.6 \, J \, cm^{-2}$), the magnitude of χ_{min} before etching decreases because the thickness of the cadmium layer decreases. However, for higher energy densities, the increase in the value of χ_{min} is due to the competition between the loss of cadmium by evaporation, which

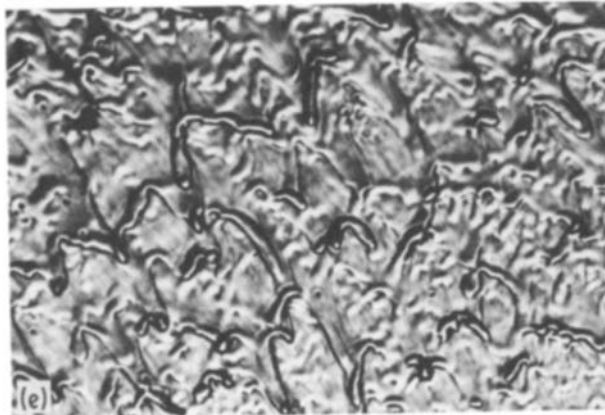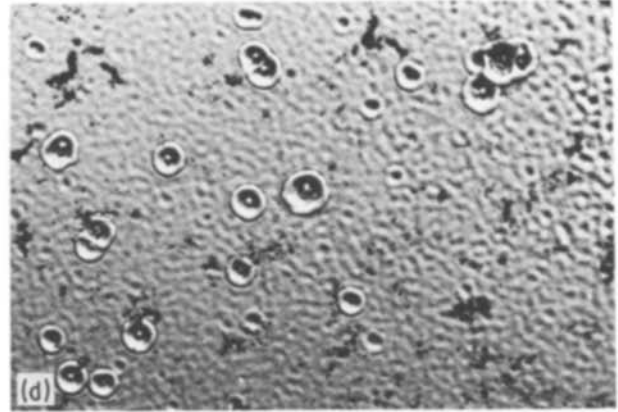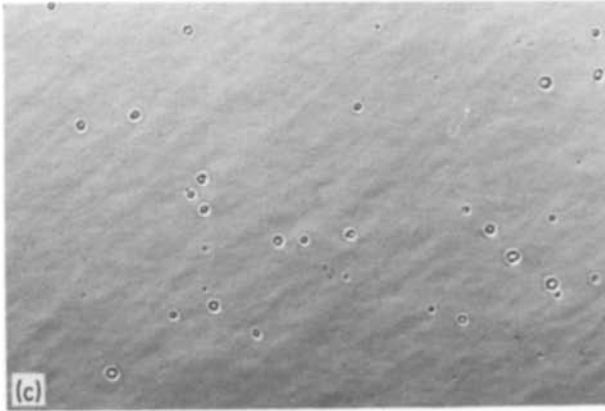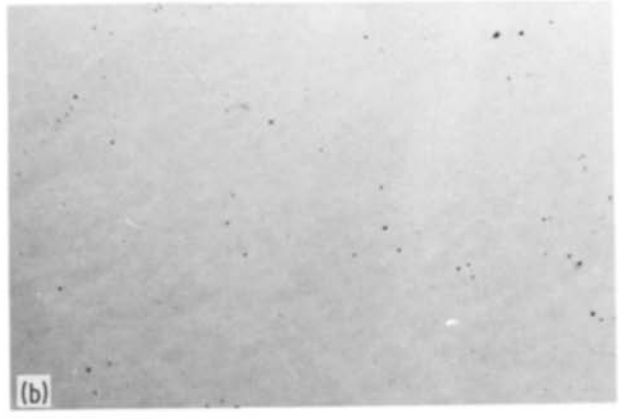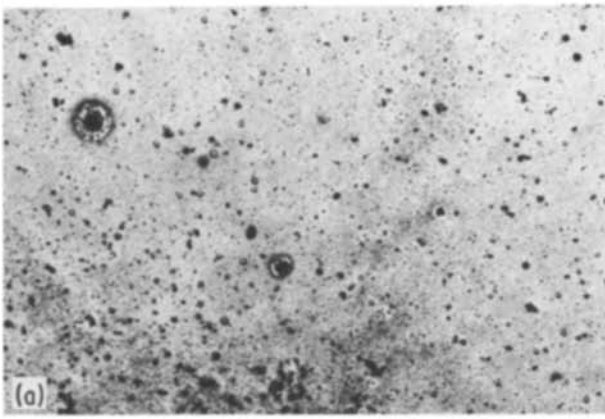*On leave from: Department Sciences des Materiaux, ENCS, 1 rue Blaise Pascal, Strasbourg, France.

Figure 1 Micrographs of Cd/GaAs annealed at different energy densities: (a) $0.2\,J\,cm^{-2}$, without etching; (b) $0.2\,J\,cm^{-2}$, (c) $0.4\,J\,cm^{-2}$, (d) $1\,J\,cm^{-2}$, (e) $1.5\,J\,cm^{-2}$, (b) to (e) etched.

tends to reduce the value, and the damage introduced by the laser into the GaAs surface, which increases the value of χ_{min}. This damage introduction manifests itself by an increase in χ_{min} after etching with increasing energy density (Table I).

For etched material, the RBS aligned spectra of Fig. 3 (left-hand side) shows that the gallium and arsenic peaks can be resolved up to energy densities of

TABLE I Relative concentration of cadmium and values of χ_{min} before and after etching

	Energy density ($J\,cm^{-2}$)			
	0	0.6	0.8	1.6
Relative concentration of cadmium between channels 400 and 430 ($\times 10^3$ counts)	110	35	32	18
χ_{min} before etching (%)	55	28	31	41
χ_{min} after etching (%)	6.0	7.5	8.0	17

at least $1\,J\,cm^{-2}$, which indicates that the GaAs is not decomposing significantly. For an energy density of $1.6\,J\,cm^{-2}$, there seems to be an excess of gallium present presumably because arsenic was lost during annealing. At the same time, the value of χ_{min} (Table I) increases correspondingly, indicating the introduction of damage by the laser for energy densities equal to or greater than $0.6\,J\,cm^{-2}$.

On the right-hand side of Fig. 3 is presented the aligned and random spectra corresponding to cadmium. In comparison with non-etched material, it is seen that cadmium has been removed by etching and that the majority of the remaining cadmium occupies lattice sites within the GaAs. That is, the yields in the aligned spectra are very small compared with the yields from random spectra. The ratio of these two yields (aligned/random) gives the fraction of cadmium interstitial atoms within the GaAs (see Table II). The decrease in substitutionality at high energy densities is thought to be related to the introduction of damage by the laser. The concentration of cadmium within the GaAs has been estimated to vary between about 5×10^{19} and $2 \times 10^{20}\,atom\,cm^{-3}$ for the spectra shown in Fig. 3.

3.3. Electrical measurements
3.3.1. Four-point probe
The values of sheet resistivity for laser irradiated samples before and after etching are shown in Table III. The increase in resistivity before etching
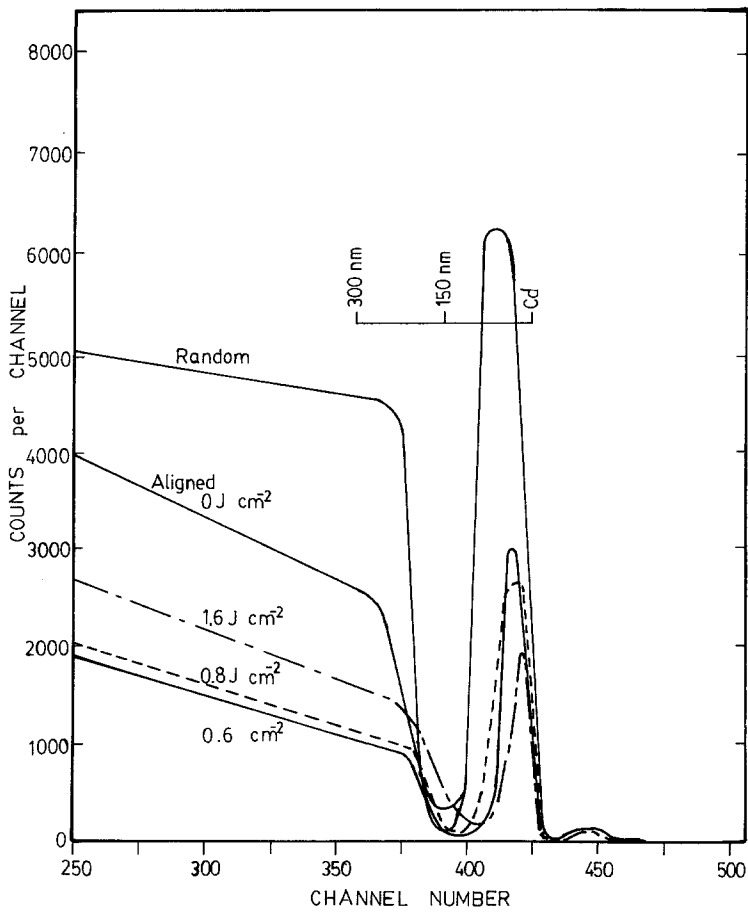
Figure 2 Rutherford backscattering spectra for samples coated with cadmium and annealed at different energy densities.
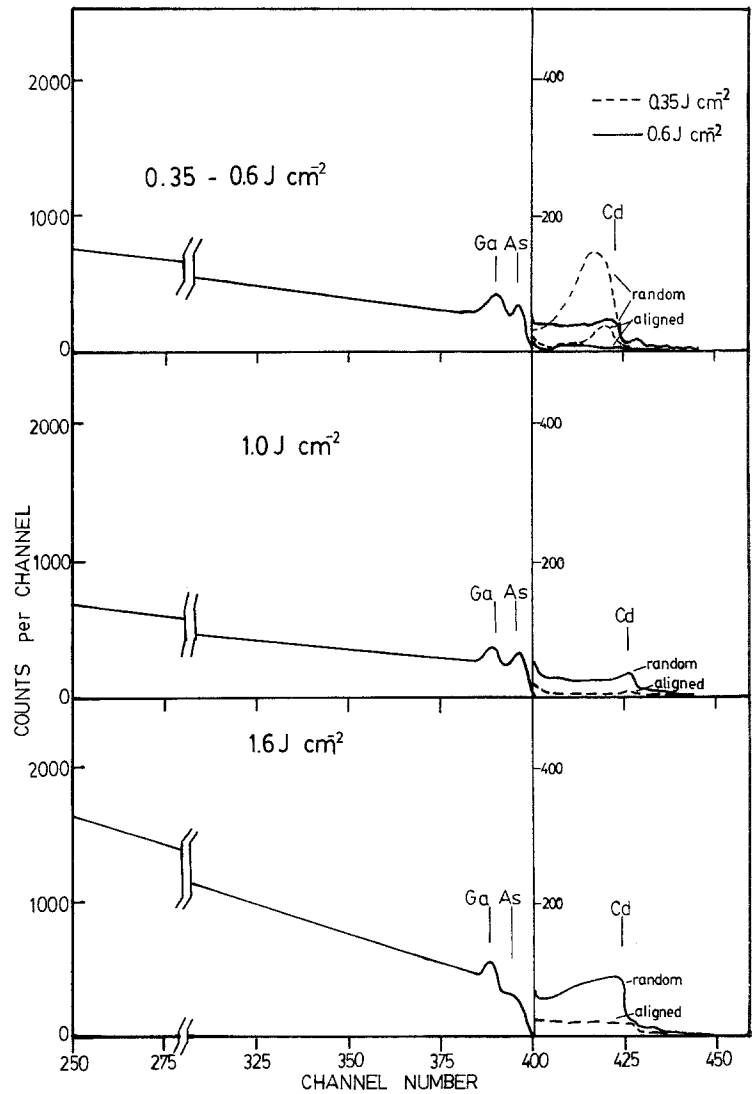

Figure 3 Rutherford backscattering spectra for Cd/GaAs etched in HCl to remove the residual cadmium after irradiation at various energy densities.
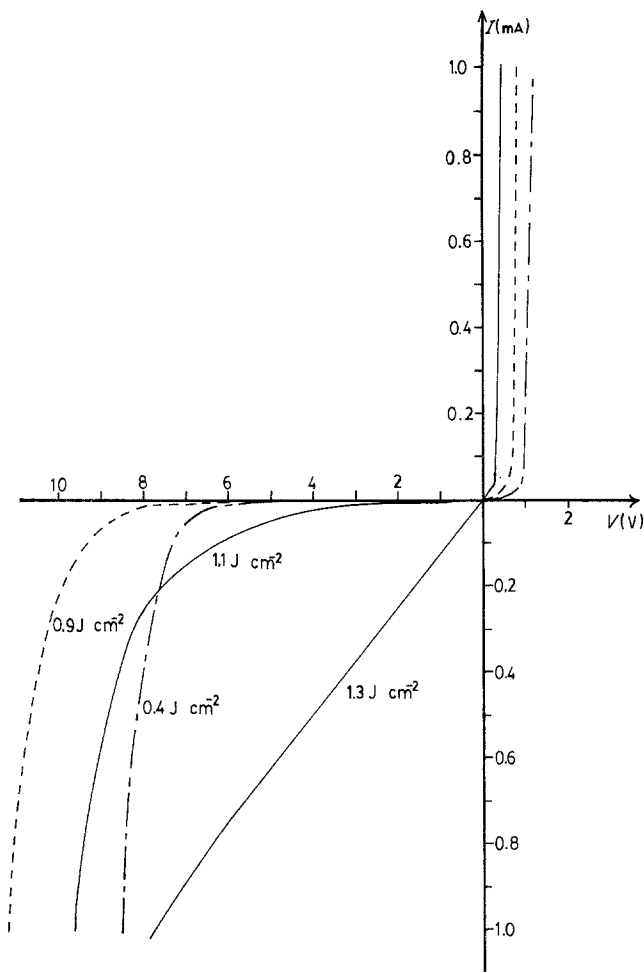
Figure 4 I–V characteristics of Cd/GaAs irradiated at a variety of energy densities.

with increasing energy density up to $1.1\,\mathrm{J\,cm^{-2}}$ indicates that an increasing amount of cadmium is lost. This effect occurs apparently without any measurable alloying of cadmium with the GaAs since the value of the resistivity after etching remains high (Table III). A significant decrease in the resistivity is obtained for energy densities greater than $1.3\,\mathrm{J\,cm^{-2}}$.

3.3.2. van der Pauw measurements

Most of the measurements performed by this method were unsuccessful either because of the high resistivity of the samples or because good ohmic contacts could not be made by evaporation of gold. The only reliable result was obtained for a sample annealed at $1.6\,\mathrm{J\,cm^{-2}}$ which had a sheet resistivity of $100\,\Omega/\square$, a mobility of $13\,\mathrm{cm^2\,V^{-1}\,sec^{-1}}$ and a sheet carrier concentration of $4.5 \times 10^{15}\,\mathrm{cm^{-2}}$. A profile of carrier concentration and Hall mobility was attempted, but after the first etch step of about $30\,\mathrm{nm}$ further measurements were impossible due to the unstable reading.

3.3.3. I–V characteristics

The I–V characteristics measured on n-type GaAs samples which had $0.5\,\mathrm{mm}$ diameter cadmium dots laser alloyed to the surface are shown in Fig. 4. The characteristic corresponding to the sample annealed at $0.4\,\mathrm{J\,cm^{-2}}$ is identical to that for an unannealed sample. For an energy density of $0.9\,\mathrm{J\,cm^{-2}}$, the breakdown voltage is largest but there is a decrease in the turn-on voltage (forward bias). At energy densities of $1.1\,\mathrm{J\,cm^{-2}}$ and above, the diode characteristics degrade (Fig. 4) which implies that they are being affected by the damage introduced by the laser.

By plotting the forward current as a function of applied voltage on a semilogarithmic plot, a value of the ideality factor, n, may be determined. The magnitude of n was found to be 4.3, 2.0, 2.3 and 3.5 for energy densities of 0.4, 0.7, 1.0 and $1.3\,\mathrm{J\,cm^{-2}}$, respectively. Thus the lowest values of n, (~ 2) are obtained for energy densities in the range 0.7 to $1.0\,\mathrm{J\,cm^{-2}}$.

4. Discussion

This work follows a similar study of laser alloyed zinc layers on GaAs [6] in which we obtained $\mathrm{p^+n}$ diodes with hole concentrations of about $1 \times 10^{21}\,\mathrm{cm^{-3}}$. The thickness of the $\mathrm{p^+}$ layer was estimated to be about $0.1\,\mu\mathrm{m}$. In contrast, the results for cadmium on GaAs presented here look rather different even though we would expect zinc and cadmium to behave similarly. The RBS measurements suggest that we should measure a high hole concentration in the range 5×10^{19} to $2 \times 10^{20}\,\mathrm{cm^{-3}}$ since the majority of cadmium atoms within the first $0.1\,\mu\mathrm{m}$ from the surface occupy lattice sites. However, the electrical properties do not seem to agree with the RBS data. Thus it is possible that many of the cadmium atoms occupy the wrong lattice sites, that is, arsenic sites rather than the gallium sites. Alternately, the cadmium atoms may form complexes with vacancies which would prevent them from acting as simple acceptors. In addition, the difficulty in obtaining reliable electrical properties may be associated with the fact that the GaAs is becoming disordered (χ_{min} increase) for energy densities above $0.6\,\mathrm{J\,cm^{-2}}$.

The four-point probe and van der Pauw measurements were carried out on SI GaAs whilst the I–V characteristics were obtained from junctions formed on n-type GaAs. Thus the degradation of the I–V characteristics cannot be responsible for the problems associated with measuring electrical properties of the p-layers on SI substrates. The apparent good results obtained following irradiation at $1.6\,\mathrm{J\,cm^{-2}}$ may be

TABLE II Percentage of cadmium on lattice sites as a function of energy density

	Energy density ($\mathrm{J\,cm^{-2}}$)				
	0.6	1.0	1.4	1.5	1.6
Number of cadmium atoms on lattice sites (%)	79	84	78	72	67

TABLE III Sheet resistivity (four-point probe) measured as a function of energy density before and after removing cadmium from the surface

	Energy density ($\mathrm{J\,cm^{-2}}$)						
	0.2	0.6	0.9	1.1	1.4	1.5	1.6
Resistivity before etching ($\Omega/\square$)	15	130	3000	10	100	25	15
Resistivity after etching ($\Omega/\square$)	HR*	HR*	$\sim 10^6$	$\sim 10^6$	240	220	32

*HR = high resistance.

influenced by the damage introduced. At this energy density it is possible that many dislocations have been introduced which trap cadmium and this can explain the increase in concentration of cadmium observed by RBS compared with values measured at lower energy densities (Fig. 3).

In a similar manner to the Zn/GaAs system, the results here suggest that nothing measurable happens to the underlying GaAs up to energy densities of $0.4 \, J \, cm^{-2}$. Above $0.4 \, J \, cm^{-2}$, the GaAs melts and much cadmium is lost by evaporation. Unlike the results for Zn/GaAs, the sheet resistivity remains high up to about $1.1 \, J \, cm^{-2}$ and it is impossible to measure reliably the electrical properties. However, the $I-V$ measurements suggest that we have formed p–n junctions whose properties are very poor. For energy densities above $1.1 \, J \, cm^{-2}$, the GaAs surface degrades (Table I) and arsenic is lost (Fig. 3). Despite this, the surface is appreciably conducting and p-type for an energy density of $1.6 \, J \, cm^{-2}$. This conductivity may be associated with the damage introduced by the laser in addition to any activity from the cadmium atoms that are present.

5. Conclusions
The laser alloying technique has been used to diffuse deposited cadmium into GaAs. The cadmium penetrates to at least $0.1 \, \mu m$ with a concentration in the range 5×10^{19} to 2×10^{20} atom cm^{-3} and with about 80% of the atoms occupying lattice sites. Despite this high substitutional component, it has not been possible to measure electrical properties reliably for cadmium on SI substrates, but $I-V$ characteristics for cadmium on n-type substrates suggest that p–n junctions have been formed. Compared with similar experiments carried out on the Zn/GaAs system which produces relatively good p$^+$n diodes, the electrical properties described in this paper are poor. Thus the Cd/GaAs system seems not to be suitable for the fabrication of p$^+$n diodes.

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